

(19) Japanese Patent Office (JP)
(20) LAID OPEN PATENTS GAZETTE (A)

(11) Laid open patent application number H1-213221
(12) Laid open August 28, 1989

(51) Int. Cl.⁴ Identification code Internal office filing number
A 61 K 7/13 7430-4C
C 08 F 8/44 MHX 7311-4J

Examination request Not requested
Number of claims 2
(Total of 7 pages [in the Japanese])

(54) Title of the invention Resin composition for fixing hair colorant and hair colorant using the same

(21) Patent application no. S63-40245

(22) Application date February 23, 1988

(72) Inventor K. Mori
4-24 Sayama Todai, Kumiyama-cho, Kuze-gun, Kyoto-fu

(72) Inventor K. Yamamoto
Shinwa Dormitory, Goou Kagaku Kogyo K.K.
58 Ijiri, Iseda-cho, Uji-shi, Kyoto-fu

(71) Applicant Goou Kagaku Kogyo K.K.
58 Ijiri, Iseda-cho, Uji-shi, Kyoto-fu

(74) Agent Patent attorney J. Ando

application
Mori
(a) maybe
(b) overlaps 5-25%
(c) overlaps 20-50%
(d) overlaps 5-20%
e
25%

Specification

1. Title of the invention

Resin composition for fixing hair colorant and hair colorant using the same

5

2. Scope of the patent claims

(1) A resin composition for fixing hair colorant, obtained by copolymerizing polymerizable monomers a to d below then neutralizing water-soluble organic basic substance

10 a. from 30 to 70% by weight of at least one monomer from acrylate esters and/or methacrylate esters represented by the following formula



15 (in the formula, R₁ is a hydrogen atom or methyl group, R₂ is a methyl group or ethyl group, and n is an integer from 1 to 10)

b. from 5 to 25% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid

c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid

d. from 20 to 50% by weight of other vinyl-based monomer.

(2) A hair colorant containing the resin composition for fixing hair colorant as claimed in claim 1.

25 3. Detailed description of the invention

Field of industrial use

The present invention relates to a resin composition for fixing hair colorant, specifically a resin composition which fixes hair colorant such as the pigments and the like used to temporarily color hair, and to a hair colorant which uses the same.

30 Prior art

Colorants for hair cosmetics such as color foams, color sprays, mascara-type agents and colorants for gray hair obtained by mixing hair colorant and resin for the fixing thereof are known agents for the temporary coloring of hair. Mascara-type agents, color sprays and color foams use ethanol, water or the like as solvent, and the color spray or color foam is loaded into a pressure-resistant aerosol vessel together with a propellant such as fluorocarbon gas.

Known examples of the abovementioned resins used for fixing hair colorants include vinylpyrrolidone-vinyl acetate copolymers, copolymers comprising methacrylate ester and monochloroacetate-modified N,N'-dimethylaminoethyl-methacrylate, and acrylate ester-methacrylate ester copolymers.

5 However, the abovementioned vinylpyrrolidone-vinyl acetate copolymer is disadvantageous in that, for example, the resulting film is hard before it absorbs moisture, and when it does absorb moisture it quickly softens and becomes sticky. Copolymers of methacrylate esters and monochloroacetate-modified N,N'-dimethylaminoethyl methacrylate are also disadvantageous in that, for example, they
10 are highly hygroscopic and there is considerable color loss when wet. Acrylate ester-methacrylate ester copolymers are also disadvantageous in that, for example, in the case of common setting agents, the resulting film is hard, flaking prevention is inadequate, there is no soft feel and hair washability is poor.

Problems to be overcome by the invention

15 Accordingly, an object of the present invention is the provision of a resin composition for fixing hair colorant, and a hair colorant using the same, which offers good hair washability, has good adhesion to hair, results in the formation of a soft film, is water resistant and does not result in color loss when rubbed.

Technical means for overcoming the problems, and use thereof

20 The inventive resin composition for fixing hair colorant is obtained by copolymerizing the following polymerizable monomers a to d then neutralizing using a water-soluble organic basic substance

a. from 30 to 70% by weight of at least one monomer from acrylate esters and/or methacrylate esters represented by the following formula

25



(in the formula, R₁ is a hydrogen atom or methyl group, R₂ is a methyl group or ethyl group, and n is an integer from 1 to 10)

30 b. from 5 to 25% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid
c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid.
d. from 20 to 50% by weight of other vinyl-based monomer;
35 moreover, the inventive hair colorant contains the abovementioned resin composition for fixing hair colorant, and hair colorant or the like.

The abovementioned monomer a improves the luster and the adhesiveness of the resin with respect to hair, and it controls hydrophilicity, hair washability and the like; the amount used is from 30 to 70% by weight, preferably from 35 to 60% by weight, with respect to the total amount of polymerizable monomer. If the amount used is less than 30% by weight, there is poor adhesion to hair, poor luster and the like, and the hair washability deteriorates, whereas if more than 70% by weight is used, the system becomes too hydrophilic and water resistance decreases.

Specific examples of monomer a include methoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytetraethylene (meth)acrylate, methoxypolyethylene glycol #400 (meth)acrylate, ethoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, ethoxytetraethylene glycol (meth)acrylate, ethoxypolyethylene glycol #400 (meth)acrylate and the like, and these acrylate esters and methacrylate esters can be used individually or combinations thereof can be used.

Monomer b also contributes to the hair washability and hydrophilicity of the resin, and the amount used is from 5 to 25% by weight, preferably from 10 to 25% by weight. If less than 5% by weight is used, the resulting film becomes sparingly soluble in water and so the hair washability will be poor, whereas if more than 25% by weight is used, moisture absorption increases and stickiness becomes marked.

As described above, unsaturated carboxylic acids chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid can be used, either individually or in combination, as monomer b.

Monomer c contributes to the water resistance and softness of the resulting film, and the amount used is from 5 to 20% by weight, preferably from 5 to 15% by weight. If less than 5% by weight is used, the film is hard and the water resistance is poor, whereas if more than 20% by weight is used, the film becomes too soft, stickiness is marked and hair washability deteriorates.

Specific examples of monomer c include 2-ethylhexyl (meth)acrylate, dodecyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate and the like, and these acrylate esters and methacrylate esters can be used individually or in combination.

Monomer d contributes to the appropriate hardness and softness and the like of the resulting film, and the amount used is from 20 to 50% by weight.

Specific examples of monomer d include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, vinylacetate, vinyl pyrrolidone, (meth)acrylamide, diacetone (meth)acrylamide, acrylonitrile, styrene and the like, and these vinyl-based monomers can be used individually or in combination.

The copolymerization of the abovementioned monomers a to d can be performed according to common solution polymerization in a hydrophilic solvent, for example, it can be performed by dissolving the monomers in hydrophilic solvent, adding polymerization initiator then agitating under a current of nitrogen at the boiling point of the solvent or a temperature close thereto. The copolymerization can proceed in the presence of the total amount of all types of abovementioned monomer from the start of the polymerization, or different types and/or amounts of monomer can be added in portions. The abovementioned solvent is preferably used such that the solids content in the resin solution is from 30 to 60% by weight.

Examples of hydrophilic solvents include C1-4 aliphatic alcohols which can dissolve in water such as methyl alcohol, ethyl alcohol, isopropyl alcohol and butyl alcohol; alcohols which contain water such as 95% ethyl alcohol; and acetone, methyl cellosolve, ethyl cellosolve, dioxane, methyl acetate, dimethylformamide and the like, and these can be used individually or in combination. It is preferable to use a peroxide such as benzyl peroxide or lauryl peroxide, or an azo-based compound such as azobisisobutyronitrile, or the like as the polymerization initiator.

By adding water-soluble organic basic substance to the resin-containing solution obtained as a result of the abovementioned copolymerization, the copolymerized resin is both neutralized and rendered water-soluble. The degree of neutralization is preferably from 50 to 100%.

Specific examples of water-soluble organic basic substances which can be used include ammonia water, mono-, di- or triethanolamine, mono-, di- or triisopropanolamine, morpholine, aminomethylpropanolamine, aminoethylpropanolamine, aminomethylpropanediol, aminoethylpropanediol and the like, and these can be used individually or in combination. When an organic amine is used, the resulting resin composition does not contain water, and this is particularly preferable in aerosols which repel water.

The resulting resin composition is such that the molecular weight of the copolymer is from around 5 000 to 200 000, and the hydrophilic solvent solution obtained as a result of the abovementioned copolymerization can either be used without further modification, or as a water-containing solvent system, in order to fix hair colorant, preferably at a (hair colorant/resin composition) ratio (solids ratio) of from (1/1) to (1/20).

Working examples 1 to 6

The present invention is described below based on working examples. It should be noted that "parts" and "percent" are based on weight.

Production of the resin composition

200 parts of polymerizable monomer a to d, 100 parts of ethanol and from 0.5 to 2 parts of polymerization initiator were introduced into a 1 l four-necked flask provided with a reflux condenser, thermometer, glass tube for nitrogen substitution, dropping funnel and agitator, and the system was heated under reflux at 80°C under a current of nitrogen for 4 hours to allow polymerization to proceed. After the polymerization, the system was cooled, an ethanolic solution of water-soluble organic basic substance was added at 50°C, and the system was diluted using ethanol to a solids content of 50%.

Table 1 shows the polymerizable monomer a to d compositions, and the types and amounts of polymerization initiator and water-soluble organic basic substances used in working examples 1 to 6 and comparative examples 1 to 6.

Table 1 Monomer composition (parts), degree of neutralization (%) and average molecular weight ($\times 1000$) of the resin

		30			20		
Monomer d	2-ethylhexyl methacrylate		20	30		5	60
Polymerization initiator	Stearyl acrylate		40	40	30	10	
Organic basic substance	Methyl methacrylate	40	40	100		55	
	Ethyl methacrylate	50	40		25	45	
	Butyl methacrylate	40	50				
	Azobisisobutyronitrile	1	1	1		1	
	Benzyl peroxide	2			2		
	Lauryl peroxide	2	1	2	2	1	2
	Monoethanolamine	19.9		19.9		10.4	41.6
	Triethanolamine		33.1	41.6		59.7	
	Ammonia water (25% aqueous solution)	41.0					
	Morpholine	21.2	28.3	10.6		28.3	
Degree of polymerization of the resin (%)	70	90	80	70	90	100	70
Average molecular weight of the resin (x1 000)	70	80	100	80	65	100	120
					75	80	60

Color base preparation

40% of the abovementioned resin composition of the comparative examples and working examples (solids content 50%) was mixed with 10% carbon black, as hair colorant, and 50% ethanol, and the color base was prepared using a three-stage roller.

Color foam preparation

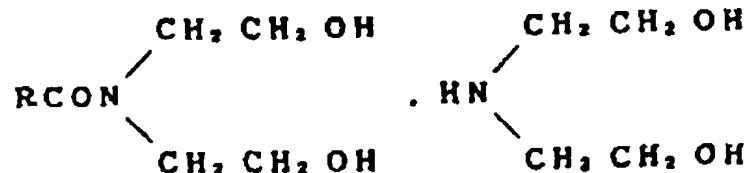
Colorants for hair comprising the three types of color foam compositions described below (type A: fast defoaming; type B: defoaming intermediate between type A and type C; type C: slow defoaming) using the abovementioned color base.

Composition (%)	Type A	Type B	Type C
Color base	10	10	10
Pullulonic-based nonionic activator *1	-	0.5	-
Fatty acid diethanolamide *2	-	-	1
Cetyl alcohol	-	-	0.1
Ethanol	60	59.4	58.9
Purified water	20	20	20
LPG (liquefied petroleum gas)	2	2	2
Fluorocarbon gas F-12	8	8	8

*1 Polyoxyethylene-polyoxypropylene block copolymer oxypropylene glycol average molecular weight 1 750,

ethylene oxide content in the whole molecule 80%

*2 Coconut oil fatty acid diethanolamide 1:2 type



Color spray preparation

Hair colorants were prepared from the color sprays having the compositions described below, using the abovementioned color base.

Composition (%)

Color base	6
Ethanol	34
Fluorocarbon gas F-11	24
Fluorocarbon gas F-12	36

(In working example 3 and comparative example 3, ammonia water was used as the organic basic substance and so it was not possible to prepare a color spray)

Mascara-type preparation

Hair colorants were prepared comprising mascara types of the following

5 composition, using the abovementioned color base.

Composition (%)

Color base	10
Resin composition (solids content 50%)	4
Ethanol	10
10 Purified water	76

Performance appraisal

An appropriate amount of the abovementioned hair colorant was applied to 10 cm decolored hair samples of approximately 1 g, the samples were dried using a drier (warm air) then the hair was appraised as described below, and the results are shown in Table 2.

(1) Stickiness

The stickiness of the hair after drying was appraised by touch to the fingers

O: Not sticky

20 Δ: Slightly sticky

x: Very sticky

(2) Flaking

Whether or not the resin fell off when the hair was combed after drying was appraised

25 O: No fall-off

Δ: Slight fall-off

x: Considerable fall-off

Table 2 Performance appraisal

		Working example						Comparative example					
		1	2	3	4	5	6	1	2	3	4	5	6
		Part	Part	part	part	part	part	part	part	part	part	part	part
Type A	Stickiness	O	O	O	O	O	O	O	Δ	Δ	O	Δ	
	Flaking	O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
	Washability	O	O	O	O	O	O	X	Δ	O	X	O	X
	Water resistance	O	O	O	O	O	O	O	X	Δ	O	X	O
Color foam	Wear resistance	1	1	1	1	1	1	2	2	3	3	3	2
	Stickiness	O	O	O	O	O	O	O	Δ	Δ	O~Δ	Δ	
	Flaking	O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
	Washability	O	O	O	O	O	O	X	Δ	O	X	O	X
Type C	Water resistance	O	O	O	O	O	O	O	X	Δ	O	X	O
	Wear resistance	1	1	1	1	1	1	2	2~3	3	3	2	
	Stickiness	O	O	O	O	O	O	O~Δ	Δ~X	Δ	Δ	Δ	
	Flaking	O	O	O	O	O	O	O~Δ	O	O~Δ	O	Δ~X	O

	Stickiness	O	O	-	O	O	O	O	Δ	-	Δ	O	Δ
Color	Flaking	O	O	-	O	O	O	Δ	O	-	O	Δ	O
Spray	Washability	O	O	-	O	O	O	X	Δ	-	X	O	X
	Water resistance	O	O	-	O	O	O	O	X	-	O	X	O
	Wear resistance	1	1	-	1	1	1	2	2	-	2	2	2
Mascara	Stickiness	O	O	O	O	O	O	O	Δ	Δ	O	Δ	O
Type	Flaking	O	O	O	O	O	O	Δ	O	Δ	O	Δ	O
	Washability	O	O	O	O	O	O	X	Δ	O	X	O	X
	Water resistance	O	O	O	O	O	O	O	X	Δ	O	X	O
	Wear resistance	1	1	1	1	1	1	3	3	3	3	3	3

(3) Washability

A 1% aqueous solution of commercial shampoo was prepared, and hair which had already been dried was washed at 35°C, then rinsed using water and dried, then the extent of fall-off was appraised.

5 O: No residue
Δ: Small amount of residue
x: Large amount of residue

(4) Water resistance

10 Hair which had been dried was immersed in water at 40°C for 30 s then removed, dried by hand using a white cloth, and the deposition of color onto the white cloth was appraised.

O: No color deposition
Δ: Slight color deposition
15 x: Considerable color deposition (part dissolved)

(5) Wear resistance

An abrasion fastness meter (JIS P-8136) was used: white cotton cloth was fixed to a table and hair that had been dried was fixed above, and abraded 30 times 20 using a 300 g load. The degree of color loss onto the white cloth was appraised from 1 to 5

1: Almost no coloration
5: Coloration of the whole surface

25 Advantages of the invention

As described above, the present invention provides a resin composition for fixing hair colorant which has excellent adhesion to hair, results in a soft film, with no stickiness or flaking, and results in excellent washability, water resistance and abrasion resistance, and provides the hair colorant obtained using the same.

30

Patent applicant Goou Kagaku Kogyo K.K.
Agent Patent attorney J. Ando

Procedural Amendment Form (Voluntary)

May 22, 1989

5 Director General of the Patent Office B. Yoshida

1. Indication of the case
Patent application number 040245 of 1988

2. Title of the invention
10 Resin composition for fixing hair colorant and hair colorant using the same

3. Person making the amendment
Relation to the case Patent applicant
Title Goou Kagaku Kogyo K.K.
Address 58 Ijiri Iseda-cho, Uji-shi, Kyoto-fu

15 Representative director M. Mikami

4. Agent
Name Patent attorney (8012) J. Ando
Address 5 Koyama Nishi Genjo, Kita-ku, Kyoto-shi, Kyoto-fu

5. Date amendment was ordered (voluntary)
20 6. Subject of the amendment The "Scope of the patent claims" and
"Detailed description of the invention" sections of the Specification

7. Details of the amendment See attached sheet

25 (Attached sheet)
Details of the amendment
(1) The scope of the patent claims is amended as indicated on the attached sheet.
(2) In the specification,

30
$$\begin{array}{c} R_1 \\ | \\ H_2 C = C - O - (OCH_2 CH_2)_n OR_2 \end{array}$$

is amended to

$$\begin{array}{c} R_1 O \\ | \\ H_2 C = C - C - (OCH_2 CH_2)_n OR_2 \end{array}$$

(3) In the specification, ethanol 60 59.4 58.9
 purified water 20 20 20

is replaced with

5 ethanol 20 20 20
 purified water 60 59.4 58.9

(attached sheet)

Amended scope of the patent claims

10 (1) A resin composition for fixing hair colorant, obtained by copolymerizing polymerizable monomers a to d below then neutralizing water-soluble organic basic substance

a. from 30 to 70% by weight of at least one monomer from acrylate esters and/or methacrylate esters represented by the following formula



(in the formula, R_1 is a hydrogen atom or methyl group, R_2 is a methyl group or ethyl group, and n is an integer from 1 to 10)

20 b. from 5 to 25% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid

c. from 5 to 20% by weight of at least one monomer from C8-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid

d. from 20 to 50% by weight of other vinyl-based monomer.

25 (3) A hair colorant containing the resin composition for fixing hair colorant as claimed in claim 1.

Agent

Patent Attorney J. Ande